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Fluids Under Extreme Conditions of Pressure and Temperature and their Role in Geological Processes

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The knowledge of phase equilibria and geomaterials properties is essential for understanding the complex physics and chemistry of the Earth. Among the different geomaterials, fluids play a crucial role in many geological processes, but their behaviour at the conditions of the Earth's interior, i.e. at high pressures P and high temperatures T, is not well known. We use *ab initio* molecular dynamics (AIMD) simulations to study the atomic structure and dynamics of such fluids to complement experimental approaches. The simulations do not only help to interpret experimental data but they can predict material behaviour under conditions not accessible to experiment. Due to the substantial computational demand of AIMD simulations, this method has only become feasible with the use of supercomputing facilities.

1 Introduction

Geomaterials, i.e. minerals, melts and volatile fluids, exhibit complex atomic structures. Whereas the Earth's core is supposably composed mainly of metallic iron, the crust and mantle consist mainly of silicates and oxides[1]. Different types of atomic structures and particle interactions pose a great challenge for computer modelling in Geomaterials Science. The substantial increase in computing power during the last decades provides the base for a realistic modelling of geologically relevant materials and processes. A first prerequisite for atomic-scale modelling is an accurate and reliable representation of the particle interactions. Electronic structure methods, e.g. using density functional theory (DFT)[2,3], have proven reliable in this respect since they are transferable between many different types of materials. However, they are computationally very demanding which limits the maximum system size, i.e. number of atoms in the simulation cell, and time scales for dynamic simulations. With the availability of supercomputing facilities, *ab initio* molecular dynamics (AIMD) simulations have become feasible. This provides access to chemically complex systems that are not well described by classical interaction potentials.

We are interested in properties of geomaterials and geological processes at conditions of the Earth's interior, i.e. at high pressure and high temperature. Generally, geologic formations are complex composites of different crystalline (minerals) and disordered (melts, glasses, fluids) materials. Their properties are ultimately determined by the bulk properties of the individual constituents and by the interfacial properties at phase boundaries. Both aspects are subject of our research. Especially for melts and fluids, experimental studies under these extreme conditions are very difficult, and important data, e.g. on the atomic structure and dynamics, are still missing. Molecular modelling is a powerful complementary approach, by which structural and physical properties may be studied simultaneously.

Melts and fluids are especially important for processes in the Earth's crust and upper mantle, which is illustrated in figure 1. When an oceanic plate is subducted beneath the

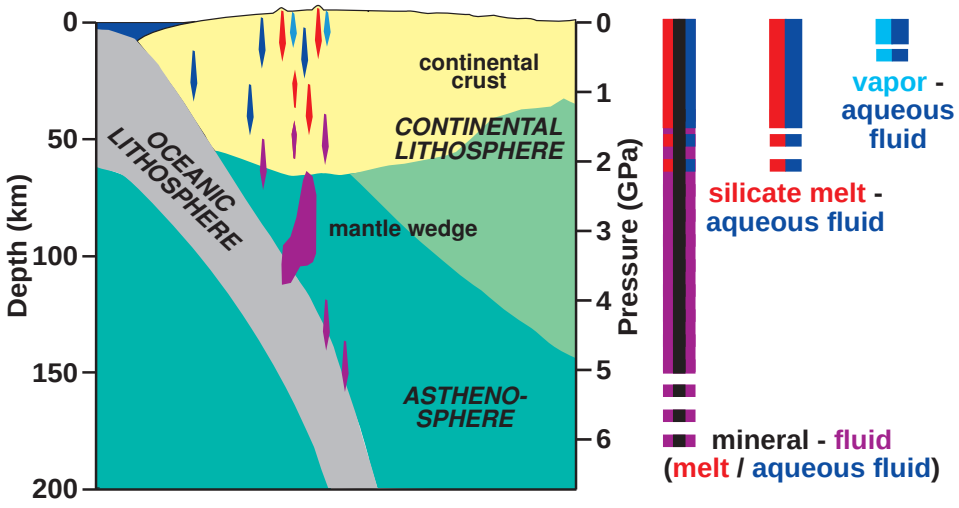

Figure 1. Schematic cross-section through the subduction zone of the Central Andes. Fluids are released at depth due to mineral phase transformations, in particular dehydration reactions, at high pressure and high temperature. The ascending fluids interact with the rocks of the mantle wedge and the continental crust, which leads e.g. to magma formation, volcanism and hydrothermal ore deposit formation.

continental crust, P and T increase with depth. As a result, water and other volatiles are released when low $P-T$ minerals become instable and transform into high $P-T$ phases. The ascending volatiles then cause a partial melting of the mantle wedge or the continental crust. Eventually, fluids and magmas reach the surface again, e.g. during volcanic eruptions. The most important water-bearing liquids of this process contain substantial amounts of silicate and/or electrolyte components. Due to the much lower viscosity, the latter type of fluid is more easily accessible by AIMD. Recently, we have studied the speciation of ions and molecules in aqueous fluid at high pressure and high temperature using supercomputing facilities at NIC Jülich and GFZ Potsdam. The results of these studies will be used to develop a better understanding of the role of fluids on geochemical processes and physical properties of geomaterials.

2 Simulation Method and Usage of HPC Facilities

For a reasonable representation of melt or fluid structure, the simulation cells have to contain at least a few hundred non-identical atoms. Even at high temperature where equilibration is relatively fast, simulation times of at least a few picoseconds are required to obtain converged averages of structural properties. Long simulation times are especially needed when properties of species with low concentration are studied, as for instance ions in solution. The electronic structure calculations are based on density functional theory (DFT) using planewave basis sets[4] as implemented in the CPMD code[5]. The Car-Parrinello MD simulations are performed with a fictitious electron mass of 600 a.u.[6], time steps of 0.12 fs and the BLYP exchange-correlation functional[7,8]. Periodic boundary conditions are applied to represent a bulk system. The CPMD code is used by a number of groups on the

NIC supercomputers JUMP and JUBL and shows good scaling behaviour up to at least 512 processors for the type of calculation that is performed within this project.

In the next section we will present results of two case studies with different system size. The first set of simulations is performed on systems with 64 water molecules and one LiF (or LiOH). Hence the total number of particles is 194 (195), respectively. A typical CPMD calculation with 10000 time steps (corresponding to a time of 1 ps) takes about 19 hours on 32 processors on JUMP. After equilibration, a minimum of five to ten picoseconds are needed to get reasonable averaging, i.e. about one week of continuous computing time for one state point. Using 512 processors on JUBL, 10000 time steps run in about two hours, which gives a speed-up of about 10 although the code runs slightly slower on JUBL than on JUMP using the same number of processors. Comparing the time needed for a single CPMD time step on JUBL, the code scales very well (see table 1).

np	real time [s]	CPU seconds
32	7.30	234
128	2.11	270
512	0.72	369

Table 1. Scaling behaviour with number of processors (np) on JUBL. The times given refer to one CPMD time step of the 194 atom simulation cell (64 H_2O + 1 LiF) at ambient conditions.

In the second study, a considerably larger number of particles is used. The corresponding simulation cell contains 120 H_2O and 4 $MgSO_4$ molecules, which gives a total of 384 atoms. A single CPMD time step takes between 4.65 s and 6.26 s of real time on JUBL using 512 processors, depending on the specific P/T conditions.

3 Atomic Structure of High Pressure Fluids

3.1 Li^+ Coordination Change in Aqueous Fluid with Pressure

A key parameter for a quantitative understanding of fluid properties and their influence on geological processes is the structural arrangement of particles in the fluid. This includes the structure of the majority species or solvent but also the complexation of minority species or solutes. Simple model systems for lithospheric fluids are dissolved salts in aqueous solutions. These systems are quite well known at ambient conditions but not at high P and T. We have used AIMD simulations to study the hydration of a Li cation in H_2O fluid in the NVT ensemble[9]. All simulations are run at constant temperature ($T = 1000\ K$). The pressure is adjusted by changing the volume (density) of the cubic simulation cell according to the equation of state of pure H_2O fluid. As already mentioned above, the simulation cells contain 64 water molecules and one LiF (or LiOH).

The calculations show that structural changes in the fluid influence the first hydration shell of the Li ion. With increasing pressure, the average number of H_2O molecules in the first hydration layer increases considerably from of about three at the lowest simulation pressure (0.3 GPa) to about five at 6 GPa. The distribution of coordination numbers at these two conditions is shown in figure 2. Since there is only a single Li ion in the simulation cell it is apparent that the hydration shell is not a static structural feature but it is

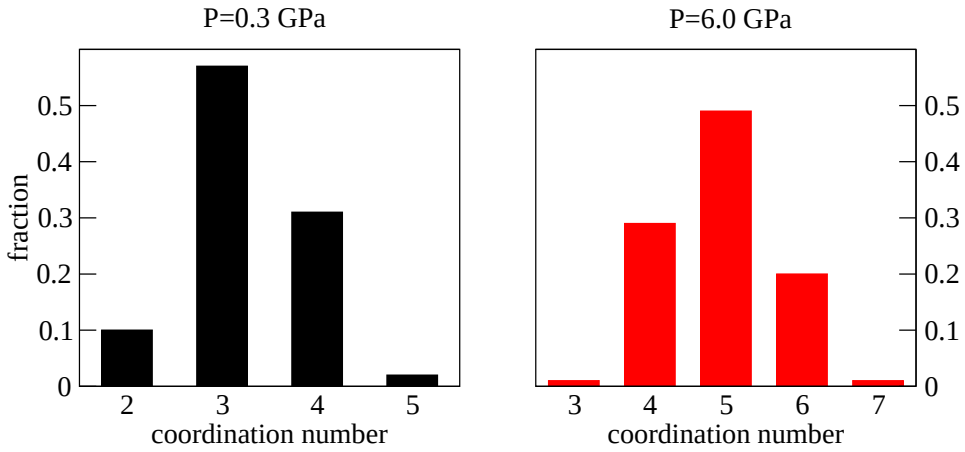

Figure 2. Distribution of the number of anions in the nearest neighbour coordination shell of the Li ion at two different pressures.

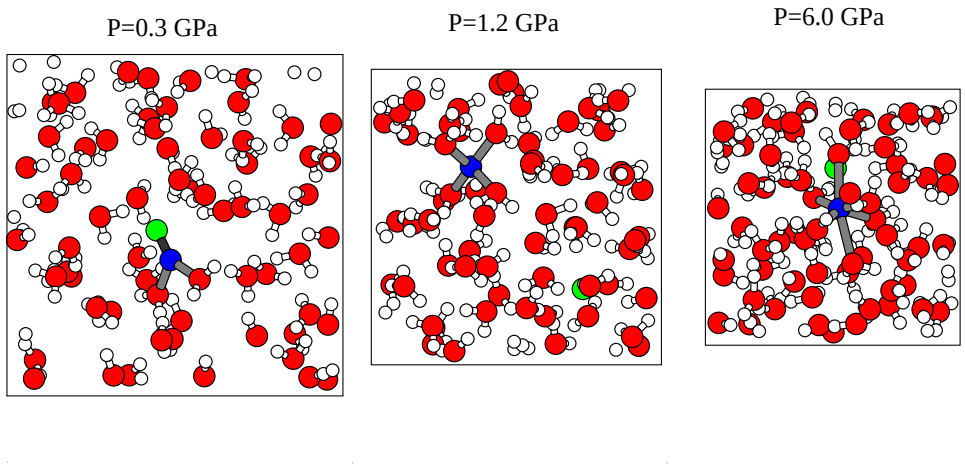

Figure 3. Snapshots from the AIMD simulations demonstrating the increase of Li coordination with increasing pressure. Grey bonds are shown between the Li and the anions of the nearest neighbour shell. Color code: Li-blue, O-red, H-white and F-green.

subject to fast dynamic changes even on the short time scale of AIMD. In figure 3 a few snapshots from the AIMD simulations at different pressures are shown. The compression of the simulation cell with increasing pressure and the increase in Li coordination is readily identifiable. An interesting observation is the tendency of association of LiF or LiOH at low pressures whereas the neutral complexes dissociate at high pressures, which is in qualitative agreement with experiment.

The results of these studies may have impact on the understanding of the geochemical cycles of light elements. For example, the Li^+ coordination change in the fluid has an

effect on the isotopic fractionation between Li-bearing minerals and fluid at high pressure. Experimental studies suggest that different local coordinations in the mineral phases lead to different trends in the fractionation behaviour[10] but so far the pressure induced structural changes are not considered in the geochemical models.

3.2 Speciation of Dissolved $MgSO_4$ in Aqueous Fluid

While the previous study was focused on the hydration of a single ion, real fluids often contain larger ionic or molecular species. Moreover, thermodynamic modelling requires a representative sampling of configurational space, which may be difficult to obtain using single ions. However, the modelling of molecular complexation or polymerization requires much larger simulation cells and hence computing power. In a pilot study we are currently investigating complexation of $MgSO_4$ dissolved in aqueous fluid. This study is in close collaboration with spectroscopists and involves the dissociation and association process of molecular species as a function of pressure and temperature and their relation to the liquid-liquid transition in H_2O fluid.

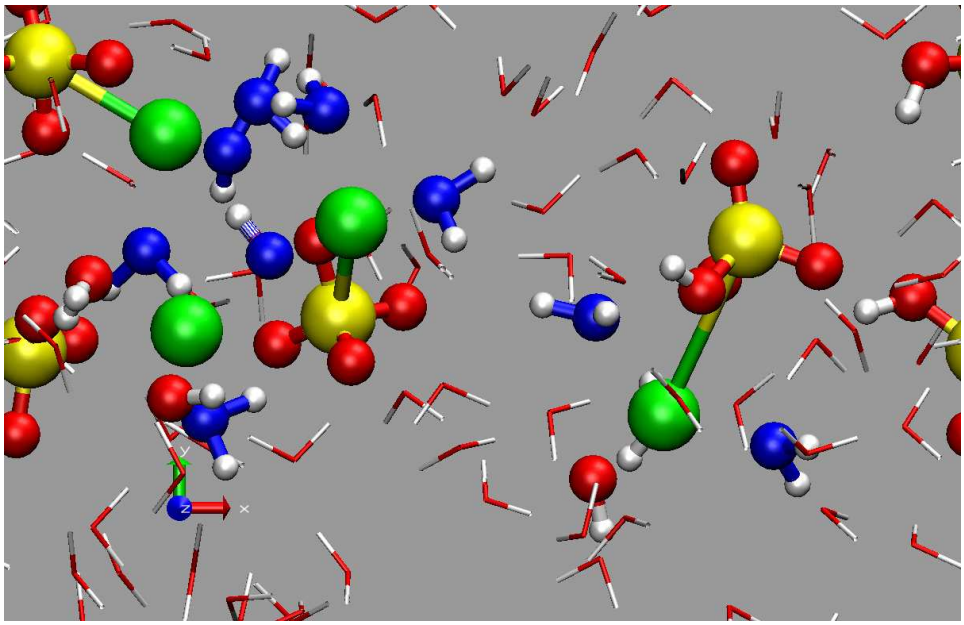

Figure 4. Snapshot from an AIMD simulation of magnesium sulfate in aqueous solution at $T = 1000$ K and $P = 0.5$ GPa. Color code: S-yellow, O-red and blue, H-white, Mg-green. H_2O or OH^- molecules in the first Mg coordination shell are shown as balls and sticks (blue O if they are also in the first hydration shell of the SO_4^{2-} molecule). For associated $MgSO_4$ a bond between S and Mg is drawn.

The speciation of sulfates in water at ambient conditions has been subject to a number of experimental studies[11–14] and quantum chemical calculations of molecular clusters[11,15,16]. The results of the simulations have been used e.g. to identify peaks in the

Raman spectrum with molecular species in the solution[11]. It is not evident how speciation changes at high P/T. It is expected that at high temperature and low pressure ionic species tend to associate[12] and perhaps to polymerize whereas the high pressure behaviour is almost completely unknown. Figure 4 shows a snapshot of an AIMD simulation at $T = 1000$ K and $P = 0.5$ GPa. Three of the four $MgSO_4$ molecules are associated, which is consistent with the expected behaviour. In the simulation we observe some proton jumps from H_2O to SO_4^{2-} which leads to the formation of species containing $[MgOH]^+$ and $[SO_3OH]^-$. These species do not seem to occur in appreciable quantity at ambient conditions. Thus further experimental and simulation studies are needed to understand this observation.

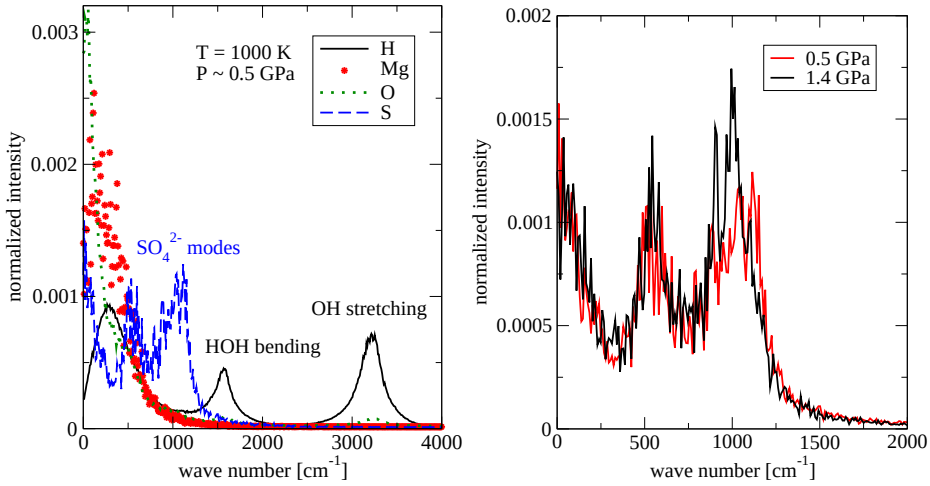

Figure 5. Power spectra of the velocity autocorrelation function representing the vibrational states of the individual species, from AIMD simulations of magnesium sulfate in aqueous solution at $T = 1000$ K. Left: Partial spectra for $P = 0.5$ GPa. Right: Partial spectrum of sulphur at two different pressures.

In order to compare with experimental data, the vibrational spectrum is calculated. Here we present the power spectra of the velocity autocorrelation function

$$z^X(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \frac{1}{3} \left\langle \mathbf{v}_1^X(0) \mathbf{v}_1^X(t) \right\rangle \exp(-i\omega t) \tag{1}$$

where $\mathbf{v}_1^X(t)$ is the velocity of a single atom of species X at time t and ω is the angular frequency. The power spectra yield the characteristic frequencies of the individual particles. In figure 5, the H spectrum shows peaks at wave numbers typical for OH stretching and HOH bending modes. Due to the small number of Mg and S atoms, their corresponding spectra are still quite noisy. However, comparing the S spectra at different pressures, clear differences are observed around 1000 cm^{-1}, which can be related to changes in the speciation. The shift of the spectral peak to lower wave numbers with increasing pressure indicates a tendency of the $MgSO_4$ molecules to dissociate, which is in qualitative agreement with expectations from experiment. A more quantitative analysis of the speciation requires still longer simulation runs, which are currently being performed.

4 Conclusions and Perspectives

The exploratory studies presented here have convinced us that AIMD simulations have great potential to study fluids at geologically relevant conditions and to reveal structural information that is difficult or impossible to access experimentally. These studies are needed not only for thermodynamic modelling of geological systems but they are a prerequisite for understanding the complex processes of fluid-rock interaction. The computational approach to Geomaterials research benefits greatly from HPC facilities such as NIC.

While the accuracy of DFT based simulations is well known for crystalline phases up to extreme conditions of P and T, the respective comparison between model and experiment is much more challenging for fluids and melts. This is partly due to the lack of high quality experimental data at high P and T but also due to the limited length and time scales of the simulations. It is therefore highly desirable to push the limits of both simulation and experiment to allow for maximum overlap and to make best use of the complementary nature of the two approaches.

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